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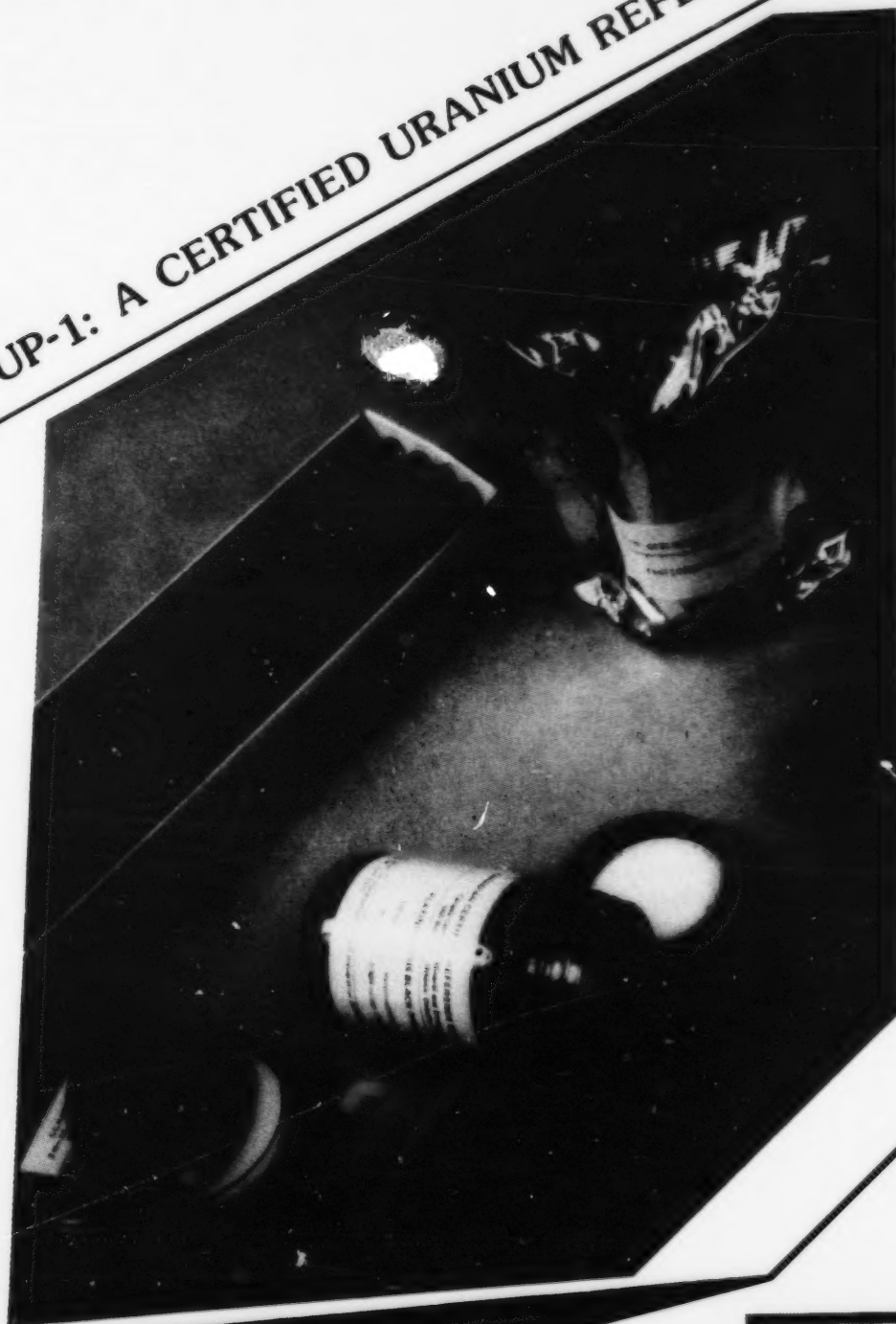
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CUP-1: A CERTIFIED URANIUM REFERENCE ORE



CCRMP 86-2E





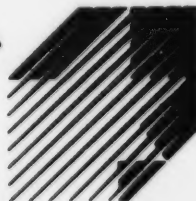
CUP-1: A CERTIFIED URANIUM REFERENCE ORE

J.L. DALTON and W.S. BOWMAN

**MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES**

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CUP-1: A CERTIFIED URANIUM REFERENCE ORE

J.L. Dalton* and W.S. Bowman**

Synopsis

Uranium in reference material CUP-1 was determined in an interlaboratory program by a variety of analytical techniques. CUP-1 was furnished by the Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee, which had arranged for the collection of the ore from the Schwartzwalder deposit, Cotter Mines, near Golden, Colorado. The Canadian Certified Reference Materials Project carried out the comminution, blending, bottling, and statistical analysis of the data produced by the Subcommittee's interlaboratory program. This reference material is thought to be in radiochemical equilibrium with members of the uranium-238 decay series.

The recommended value for uranium in CUP-1 is 0.128 wt %.

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CUP-1: UN MINÉRAI D'URANIUM DE RÉFÉRENCE CERTIFIÉ

J.L. Dalton* et W.S. Bowman**

Résumé

L'uranium dans le minéral de référence CUP-1 a été déterminé à l'aide de diverses méthodes d'analyse dans le cadre d'un programme interlaboratoires. Le CUP-1 a été fourni par le sous-comité d'analyse du Comité canadien métallurgique des producteurs d'uranium qui a organisé la collecte du minéral provenant du gîte Schwartzwalder des mines Cotter, près de Golden au Colorado. Cet échantillon de minéral a été broyé, mélangé puis embouteillé par le Projet canadien des matériaux de référence certifié qui a effectué aussi l'analyse des données fournies par le sous-comité du programme interlaboratoires. Ce matériau de référence est en équilibre radiochimique avec les membres de la série de désintégration de l'uranium 238.

La valeur recommandée d'uranium dans le CUP-1 est 0,128 % en poids.

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CONTENTS

SYNOPSIS	1
RÉSUMÉ	111
INTRODUCTION	1
INTERLABORATORY PROGRAM FOR CERTIFICATION	1
STATISTICAL TREATMENT OF ANALYTICAL RESULTS	1
Detection of outliers	1
Estimation of consensus value and 95% confidence limits	1
Criterion for certification	2
DISCUSSION	5
REFERENCES	5
APPENDIX A - CONFIRMATION OF HOMOGENEITY	7
APPENDIX B - PARTICIPATING LABORATORIES	11

TABLES

1. Gamma-ray activity ratios from a handpicked sub-sample of Lot 4	3
2. Approximate chemical composition	3
3. Particle-size analysis	3
4. Recommended value and statistical parameters (outlier excluded) for uranium	3
5. Analytical results, laboratory means, and standard deviations for uranium in CUP-1	4
6. Summary of analytical methodology (outliers excluded)	4
7. Values of σ_B/σ_A and RP for uranium in CUP-1	4
A8. Confirmation of homogeneity of CUP-1 (XRF)	9

FIGURE

1. Histogram for the distribution of results for uranium	6
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INTRODUCTION

The Analytical Subcommittee of the Canadian Uranium Producers Metallurgical Committee felt that it would be highly desirable to have a uranium reference material known to be in radiochemical equilibrium. An American radiochemist, C. Sill, had shown that the ore sample obtained by him from the Schwartzwalder deposit near Golden, Colorado, could be considered to be in such a state (1). A geological investigation attributed the radiochemical equilibrium to the environment and the ore's location below the zone of oxidation (2). Therefore, it was proposed that the Subcommittee obtain a large sample of this ore, prepare it in a manner commensurate with its end-use as a powder reference material, and carry out an interlaboratory program for uranium certification.

A uranium reference ore, which is known to be in radiochemical equilibrium, has additional intrinsic value as a compositional reference material for each of the uranium decay series isotopes. The concentration of each isotope is numerically identical to that of uranium-238, which may be accurately calculated from its concentration and known specific activity.

Accordingly, arrangements were made to collect the material from the mine in Colorado and to carry out the preparation with the facilities of the Canadian Certified Reference Materials Project (CCRMP) at CANMET in Ottawa.

The Subcommittee engaged Crystal Bay Geo-Min Services to select the ore on the site of the deposit at Cotter Mines near Golden, Colorado. Since it was not possible to obtain ore from exactly the same location as the Sill sample, four other locations were sampled. Following analytical work by the Subcommittee, Lot 4 was chosen on the basis of the results of gamma-ray activity ratios from a handpicked sub-sample as shown in Table 1. Lot 4 was obtained from the 1300 Illinois north stope in the Cotter Mine. Approximately 200 kg of Lot 4 was shipped to CCRMP in Ottawa.

CCRMP carried out all the sample preparation work, that is the comminution, blending, and bottling. The ore was ground to pass a 74- μ m

screen and bottled in 200-g units. A nominal composition of the bottled material is shown in Table 2. A particle-size analysis is shown in Table 3. CANMET'S Chemical Laboratory carried out the homogeneity test for uranium by x-ray fluorescence analysis, the details of which are presented in Appendix A.

INTERLABORATORY PROGRAM FOR CERTIFICATION

Participating laboratories in the certification program are listed in Appendix B. All are members of the Subcommittee. Each laboratory was assigned a code number that bears no relation to its alphabetical order.

Each laboratory was requested to contribute five replicate results for uranium by a method of its choice and to report the results on an "as is" basis. Some laboratories submitted more than the five results requested, and one laboratory submitted results by two different methods. In the latter case, each set was considered statistically independent. The recommended value for CUP-1 is presented in Table 4. Analytical results, laboratory means, and standard deviations are presented in Table 5; methodological information is presented in Table 6.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

There were no sets of results whose means differed from the overall mean by more than twice the overall standard deviation. However, Cochran's Test (3) revealed that Laboratory 8 had high variance, and Dixon's Test (3) applied to this set of results indicated a single low value was the cause. This value was not used in subsequent computations.

ESTIMATION OF CONSENSUS VALUE AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and variance. This approach considers the results of the described certification program to be only one sam-

pling out of a universal set of results. The analytical data were assumed to fit the model (3)

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i ,
 μ = the true consensus value,
 y_i = the discrepancy between the mean of the results in the set i ($\bar{x}_i$) and μ ,
 and
 e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i$.

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2 , respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares, with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}_{..}$ by:

$$\bar{x}_{..} = \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} x_{ij}}{\sum_{i=1}^k n_i}$$

where n_i = the number of results in set i , and
 k = the number of sets.

The value of σ^2 is estimated by s_1^2 , which is given by

$$s_1^2 = \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2}{\sum_{i=1}^k n_i - k}$$

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) / \frac{1}{k-1} \left(\sum_{i=1}^k n_i - \frac{\sum_{i=1}^k n_i^2}{\sum_{i=1}^k n_i} \right)$$

where

$$s_2^2 = \frac{\sum_{i=1}^k n_i (\bar{x}_i - \bar{x}_{..})^2}{k-1}$$

The variance of the overall mean is given by

$$V(\bar{x}_{..}) = \left(\frac{k}{\sum_{i=1}^k n_i^2 / (\sum_{i=1}^k n_i)^2} \right) \omega^2 + \left(\frac{k}{1 / \sum_{i=1}^k n_i} \right) \sigma^2$$

and the 95% confidence limits for $\bar{x}_{..}$ are

$$\bar{x}_{..} \pm t_{0.975, (k-1)} \sqrt{V(\bar{x}_{..})}$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 instances would fall within the prescribed limits.

The average within-set standard deviation, σ_A , is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists, therefore, that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A .

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A , where

$$\sigma_B = \sqrt{\frac{k}{\sum_{i=1}^k (\bar{x}_i - \bar{x}_{..})^2 / (k-1)}}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (4). The acceptable upper limit for σ_B/σ_A is 2 for uranium.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%. The values of σ_B/σ_A and RP for CUP-1 are reported in Table 7. CUP-1 meets the certification criterion of $RP < 15\%$ for $\sigma_B/\sigma_A \leq 2$ as required for uranium.

Table 1 - Gamma-ray activity ratios from a handpicked sub-sample of Lot 4*

Ra-226/U-238	1.004
Pb-214/U-238	1.002
Bi-214/U-238	1.003
Bi-214/U-238	0.997

*Source of Lot 4 in the Schwartzwalder deposit, Cotter Mine, is the 1300 Illinois north stope.

Table 2 - Approximate chemical composition

Component	Mass %
Na ₂ O	0.2
MgO	4.7
Al ₂ O ₃	7.9
SiO ₂	39
S	1.2
K ₂ O	6.4
CaO	10
TiO ₂	0.5
MnO	0.7
Fe ₂ O ₃	12
ZnO	0.1
MoO ₃	0.1

Table 3 - Particle-size analysis

Size of fraction (μm)	wt %
-104 + 74	0.0
-74 + 46	11.4
-46 + 37	20.5
-37	68.1

Table 4 - Recommended value and statistical parameters (outliers excluded) for uranium

No. of laboratories	No. of sets of results	No. of results	Overall mean	95% CL		σ _A
				Low	High	
9	10	60	0.128	0.126	0.130	0.0023

Table 5 - Analytical results, laboratory means, and standard deviations for uranium in CUP-1

Laboratory	Method	Results, uranium (wt %)					Mean	S.D.
Laboratory 1 (Fluor)		0.12873	0.12830	0.12975	0.12890	0.12898	0.1289	0.0005
Laboratory 2 (Color)		0.1290	0.1284	0.1356	0.1242	0.1298	0.1294	0.0041
Laboratory 3 (Fluor)		0.1255	0.1280	0.1280	0.1289	0.1340	0.1310	0.0052
		0.1348	0.1323	0.1255	0.1331	0.1238		
		0.1399	0.1382					
Laboratory 4 (Fluor)		0.1310	0.1300	0.1277	0.1280	0.1331	0.1300	0.0022
Laboratory 5 (NAA)		0.1230	0.1240	0.1230	0.1250	0.1230	0.1236	0.0009
Laboratory 6 (Fluor)		0.1303	0.1318	0.1305	0.1320	0.1314	0.1312	0.0008
Laboratory 7 (Color)		0.131	0.130	0.128	0.127	0.129	0.1290	0.0016
Laboratory 7 (Fluor)		0.132	0.126	0.126	0.128	0.123	0.1270	0.0033
Laboratory 8 (Fluor)		0.122	0.124	0.122	0.114*	0.122	0.1228	0.0050
		0.121	0.125	0.132				
Laboratory 9 (XRF)		0.1273	0.1269	0.1280	0.1271	0.1270	0.1273	0.0004
		0.1273						

* Declared outlying value.

Table 6 - Summary of analytical methodology (outliers excluded)

Method	Decomposition, separation, etc.	Laboratory No.	n	$\bar{x}$ (wt %)
Fluorimetry	Multi-acid	1, 3, 6, 7, 8	34	0.129
	Multi-acid + fusion	4	5	0.130
Colorimetry	Multi-acid + fusion; uranium extracted with TOPO into cyclohexane; color developed with bromo-padap	2, 7	10	0.129
Neutron activation analysis	Delayed neutron counting	5	5	0.124
X-ray fluorescence	Fusion with $Li_2B_4O_7$.LIF to produce glass disc	9	6	0.127

Table 7 - Values of σ_B/σ_A and RP for uranium in CUP-1

σ_B/σ_A	RP(%)
1.2	0.0

DISCUSSION

Table 6 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separations, and determination steps. The excellent agreement between methods is readily apparent.

Figure 1 illustrates the plot of the relative frequency of occurrence against the concentration levels for uranium. The observed distribution shows the consensus attained by the participating laboratories.

REFERENCES

1. Sill, C.W. "Determination of thorium and uranium isotopes in ores and mill tailings by alpha spectrometry"; *Anal Chem* 49:4:618-621; 1977.
2. Rosholt, J.N.; Butler, A.P.; Garner, E.L.; and Shields, W.R. "Isotopic fractionation of uranium in sandstone, Powder River Basin, Wyoming and Slick Rock District, Colorado"; *Econ Geology* 60:199-213; 1975.
3. Brownlee, K.A. *Statistical Theory and Methodology in Science and Engineering*; John Wiley and Sons, Inc.; New York; 1960.
4. Steger, H.F. "A re-assessment of the criterion for certifiability in CCRMP"; *Geostandards Newsletter* VI: 17-23; 1982.

REFERENCE MATERIAL CUP-1

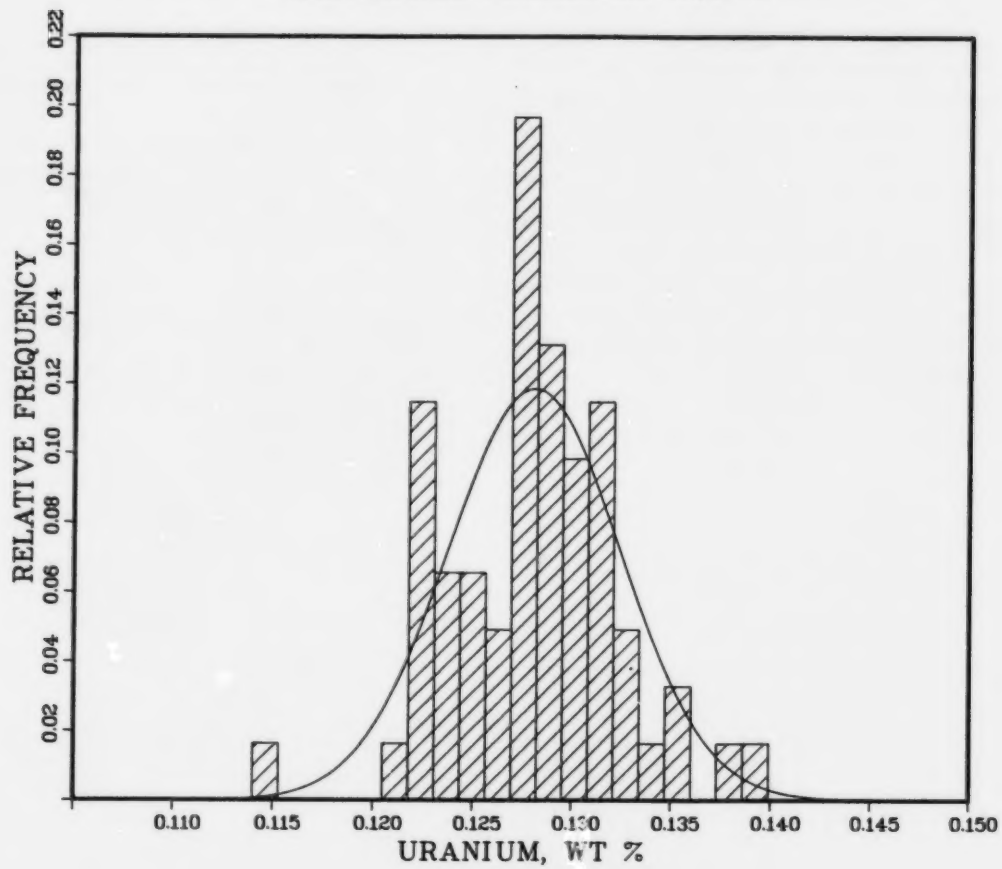


Fig. 1 - Histogram for the distribution of results for uranium

APPENDIX A

CONFIRMATION OF HOMOGENEITY

CONFIRMATION OF HOMOGENEITY

The homogeneity of CUP-1 was assessed with respect to uranium by x-ray fluorescence analysis performed at CANMET. This was done by counting triplicate aliquots from 15 bottles selected from a stock of 750 bottles. The stock was divided into 15 lots of 50 bottles. The code number of the first bottle was selected at random out of the first lot. The code number of the remaining bottles selected was given by the code number of the preceding bottle plus 75. The results are shown in Table A8.

A Spex XRF plastic cup was completely filled with the material (approximately 5 grams), and a Mylar film was used to cover the cell, which was in the inverted position during the XRF measurement. The uranium L alpha line at $37.30^\circ 2\theta$ for the LiF_{220} crystal was used for the measurement.

Table A8 - Confirmation of homogeneity of CUP-1 (XRF)

Bottle No.	Counts per second			Mean
	Individual			
7	2480	2481	2489	2483.33
57	2495	2511	2469	2491.67
107	2481	2471	2489	2480.33
157	2498	2485	2473	2485.33
207	2507	2510	2492	2503.00
257	2492	2501	2490	2494.33
307	2494	2510	2469	2491.00
357	2481	2468	2510	2486.33
407	2488	2473	2499	2486.67
457	2484	2494	2466	2481.33
507	2484	2478	2461	2474.33
557	2493	2469	2500	2487.33
607	2499	2502	2499	2500.00
657	2481	2474	2488	2481.00
707	2514	2478	2510	2500.67
Overall mean is				2488.44

Analysis of variance

Source of variation	Degrees of freedom	Sum of squares	Mean squares
Between-sets	14	.28857778E+04	.20612698E+03
Within-sets	30	.58953333E+04	.19651111E+03
Total	44	.87811111E+04	

Calculated F statistic = 1.049

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for uranium.

APPENDIX B

PARTICIPATING LABORATORIES

PARTICIPATING LABORATORIES

Atomic Energy of Canada Ltd.
Whiteshell Nuclear Research Establishment
Pinawa, Manitoba
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CANMET, Mineral Sciences Laboratories
Energy, Mines and Resources Canada
Ottawa, Ontario

Cluff Mining
Saskatoon, Saskatchewan
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Denison Mines Ltd.
Elliot Lake, Ontario
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